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SHORT COMMUNICATIONS

The Solubility of Light Fullerenes in Styrene over the Temperature Range 20–80°C

K. N. Semenov[a], N. A. Charykov[b], O. V. Arapov[b], and M. A. Trofimova[a]

[a] *St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199164 Russia*
[b] *ZAO "Innovations of Leningrad Institutes and Enterprises," St. Petersburg, Russia*
e-mail: semenov1986@yandex.ru

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Abstract—The temperature dependence (over the range 20–80°C) of the solubility of light fullerenes (C_{60} and C_{70}) and a mixture of fullerenes (60 wt % C_{60}, 39 wt % C_{70}, and 1 wt % $C_{76–90}$) in styrene was studied. The corresponding solubility polytherms are given and characterized.

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INTRODUCTION

The solubility of fullerenes is of importance for the development of methods for the crystallization and extraction isolation of these compounds from fullerene soot or fullerene mixtures, the selection of solvents for chromatographic and prechromatographic separation of fullerene mixtures, and studies of chemical reactions involving fullerenes [1–4].

Our interest in the polythermal dependence of the solubility of pure fullerenes and fullerene mixtures in styrene is related to the possibility of optimizing the conditions of the thermal catalytic polymerization (in the presence of benzoyl peroxide) of styrene for the preparation of polystyrene modified with fullerenes and fulleroid materials. The polymerization mechanism was suggested in [5], and a correlation between the concentration of pure C_{60} fullerene in polystyrene, polymerization temperature, and polymerization yield was established. According to [6], fullerenes and fulleroid materials very strongly influence the polymerization of various organic compounds and radically change the properties of polymers (mechanical, physicochemical, and electric). For example, it was shown [6] that the samples of caprolone modified by pure fullerenes and a mixture of fullerenes showed improved hardness, impact toughness, attrition resistance, softening and melting temperatures, moisture absorption, and moisture capacity. The modification of samples allows the electrophysical characteristics of caprolones (specific volume resistance, dielectric resistance, and tangents of dielectric losses) to be varied to a substantial extent.

EXPERIMENTAL

Studies were performed with pure C_{60} and C_{70} fullerenes (99.5 wt % pure, the content of the major impurities (C_{60} in C_{70} and C_{70} in C_{60}) was about 0.5 wt %) produced by ZAO "ILIP" (St. Petersburg), *o*-xylene of ch. d. a. (pure for analysis) grade, and styrene of ch. d. a. grade. The purity of the reagents was controlled chromatographically and by refractive index and boiling point measurements.

The polythermal solubility of pure fullerenes (C_{60}, C_{70}) and fullerene mixture (60 wt % C_{60}, 39 wt % C_{70}, and 1 wt % $C_{76–90}$) in styrene over the temperature range 20–80°C was studied by isothermal saturation. Initially, solutions of pure fullerenes and fullerene mixture in styrene were prepared (in all experiments, fullerenes were taken in large excess, 400 mg fullerenes per 20 ml styrene). The solutions were then saturated at a given temperature (20–80°C) in a temperature-controlled shaker (the temperature was maintained to within ±0.1 K) for 8–10 h at each temperature. The long duration of measurements is explained by the slow establishment of equilibria in the systems (styrene– C_{70}, C_{60}, fullerene mixture). For analyses, the solutions were separated from the solid phase by filtration on a Schott filter of porosity 10.

The concentrations after each stage of saturation with pure fullerenes C_{60} and C_{70} and fullerene mixture were determined on a Specord M-32 spectrophotometer at wavelengths λ = 335.5 and 472.0 nm. For measurements, aliquots of solutions of C_{60}, C_{70}, or fullerene mixture in styrene were taken and diluted with *o*-xylene, and a solution of styrene in *o*-xylene of the same dilution was used as a reference.

The concentrations of C_{60} and C_{70} in saturated solutions were calculated using the empirical dependences obtained for solutions in *o*-xylene [7],

$$c(C_{60}) = 13.10(D_{335} - 1.808D_{472}), \quad (1)$$

$$c(C_{70}) = 42.51(D_{472} - 0.0081D_{335}), \quad (2)$$

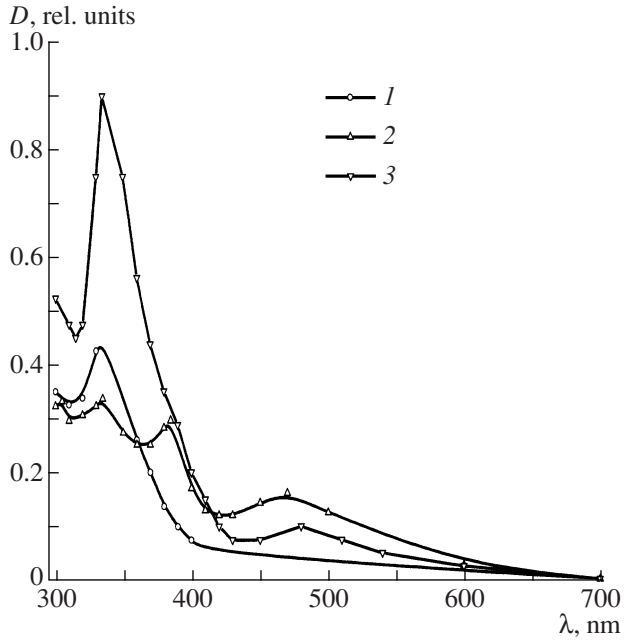

Fig. 1. Optical spectra of solutions of C_{60}, C_{70}, and fullerene mixture (dilution with *o*-xylene (1 : 700), styrene in *o*-xylene of the same dilution as a reference solution, *D* is the optical density, λ is the wavelength); (*1*) C_{60}, 4.01 g/l; (*2*) C_{70}, 4.72 g/l; and (*3*) fullerene mixture (60 wt % C_{60}, 39 wt % C_{70}, and 1 wt % $C_{76–90}$), 9.36 g/l.

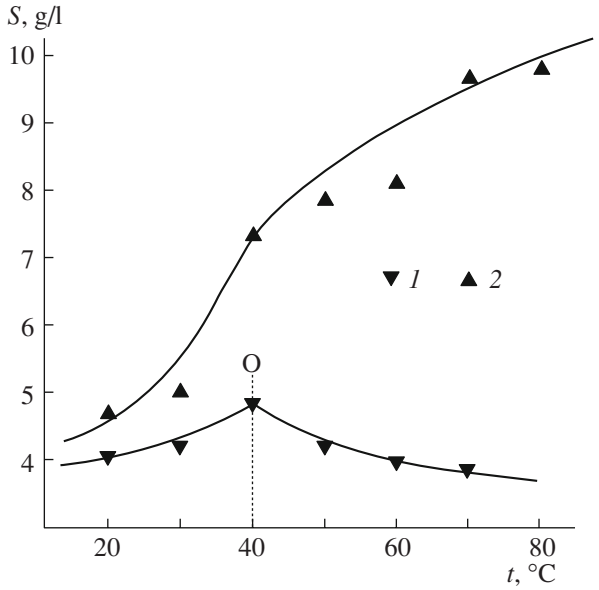

Fig. 2. Solubility polytherm of (*1*) C_{60} and (*2*) C_{70} in styrene; O is the point of monosolvate dissociation, $C_{60} \cdot 2C_6H_5CH{=}CH_2 \longrightarrow C_{60} + 2C_6H_5CH{=}CH_2$.

where D_{335} and D_{472} are the optical densities of solutions for a 1 cm thick absorbing layer and $c(C_{70})$ and $c(C_{60})$ are the concentrations of fullerenes (mg/l). Here and throughout, we ignored the presence of insignificant amounts of so-called higher fullerenes. The concentrations were determined to within ±(0.1–0.2) g/l depending on the current concentration of fullerenes.

The data on the solvent content in crystal solvates were obtained as follows: the freshly formed solid phase precipitated from the corresponding alcoholic solution was repeatedly washed with ethanol, dried at 20°C for 30 min, and weighed. The solid phase was then washed repeatedly in a Soxhlet apparatus with ethanol (78°C, 1 atm), dried in a vacuum (0.1 torr) at 200°C for 1 h, and weighed again. The change in the weight of the solid phase was used to determine the content of the solvent in the initial crystal solvate (or a solid solution of fullerenes).

RESULTS AND DISCUSSION

Figure 1 shows the electronic absorption spectra of pure fullerenes (C_{60} and C_{70}) and fullerene mixture (60 wt % C_{60}, 39 wt % C_{70}, and 1 wt % $C_{76–90}$) in styrene. Note that the spectra do not exhibit solvatochromic effects and are closely similar to the corresponding spectra in aromatic solvents (*o*-xylene, benzene, toluene, and *o*-dichlorobenzene). The use of empirical Eqs. (1) and (2) is therefore justified. Such a stability of the absorption spectra of fullerenes at λ = 335 nm with respect to solvent changes is only observed for dilute solutions; at λ = 472 nm, much more concentrated solutions are admissible.

Figures 2–4 show the polytherms of solubility of pure fullerenes (C_{60}, C_{70}) and fullerene mixture components in styrene; the polythermal data are given in the table. Different shapes of the temperature dependences of solubility attract attention: for pure C_{60} and fullerene mixture components (C_{60} and C_{70}) (Figs. 2, 3), the temperature dependences of solubility are nonmonotonic, which is direct evidence of solution through solid crystal solvate formation.

An analysis of the solid phase showed that the solid phase at equilibrium with the saturated solution on low-

Solubility of light fullerenes in styrene at 20–80°C, g/l

Fullerene	20°C	30°C	40°C	50°C	60°C	70°C	80°C
C_{60}	4.02	4.18	4.82	4.18	3.95	3.83	–
C_{70}	4.72	5.01	7.35	7.88	8.14	9.71	9.84
60% C_{60}, 39% C_{70}, 1% $C_{76–90}$	9.37	11.0	13.6	11.6	9.25	6.80	–

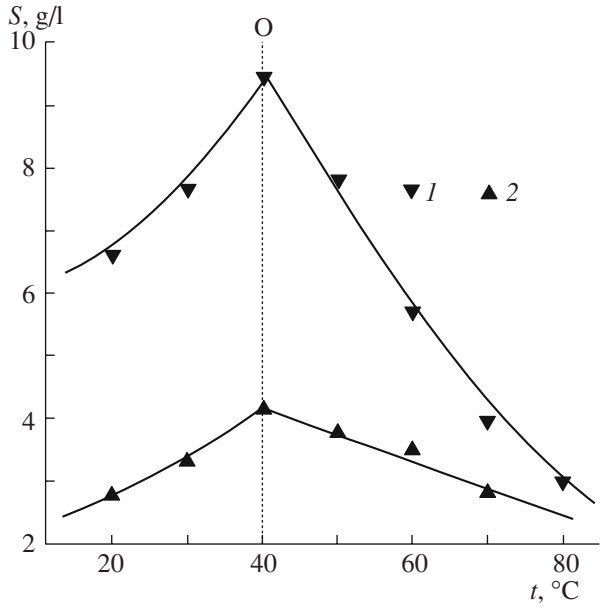

Fig. 3. Solubility polytherm of (*1*) C_{60} and (*2*) C_{70} from fullerene mixture. Here and throughout, the composition of the solid solution of fullerenes (wt %) is 60, C_{60}; 39, C_{70}; and 1, $C_{76–90}$; O is the point of bisolvated solid solution dissociation, $(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2 \longrightarrow (C_{60})_x(C_{70})_{1-x} + 2C_6H_5CH{=}CH_2$.

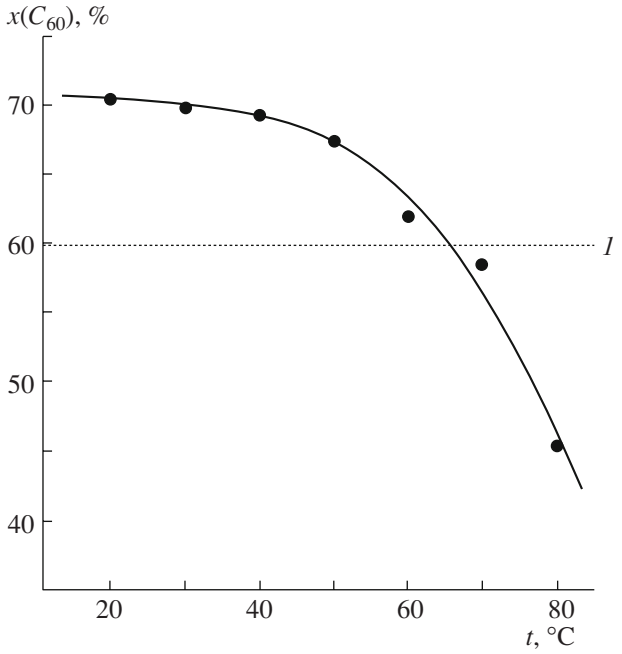

Fig. 4. Content of C_{60} in a mixture of fullerenes in saturated solution $x(C_{60})$ (wt % C_{60} from the sum of all fullerenes) as a function of temperature. Line *1* corresponds to the initial solid solution.

temperature branches of solubility polytherms (Fig. 2) is C_{60} disolvate, C_{60}–$C_{60} \cdot 2C_6H_5CH{=}CH_2$ (in the C_{60}–styrene binary system) and substitution solid solution disolvate $(C_{60})_x(C_{70})_{1-x} \cdot 2C_6H_5CH{=}CH_2$ (in the C_{60}–C_{70}–styrene ternary system); here, x is the weight percent content of light fullerenes in the solid solution. We used the solid solution consisting of 60 wt % C_{60}, 39 wt % C_{70}, and 1 wt % $C_{76–90}$.

At the nonvariant (under the constant pressure condition) point O, the crystal solvates melt incongruently with the formation of nonsolvated pure C_{60} (Fig. 2) and nonsolvated solid solution (Fig. 3). Along the high-temperature branch of the solubility polytherm, the solid phase at equilibrium with the saturated solution is nonsolvated C_{60} (for the C_{60}–styrene binary system) and nonsolvated solid solution (for the C_{60}–C_{70}–styrene ternary system).

In contrast, for the C_{70}–styrene binary system (Fig. 2), the solubility polytherm is an S-shaped curve; this is evidence that the solid phase at equilibrium with the saturated solution is nonsolvated C_{70} fullerene (otherwise, a nonmonotonic temperature dependence of solubility is as a rule observed [8–12]). The absence of crystallization styrene in the solid phase with pure fullerene C_{70} was also proved experimentally.

It should be noted that the general form of polythermal dependences (Fig. 2) is typical of light fullerenes and closely agrees with the available literature data [8–12].

An analysis of the curve of the percent content of C_{60} in styrene versus temperature (Fig. 4) shows that the content of C_{70} increases monotonically as the temperature grows. The enrichment of the liquid phase in fullerene C_{70} (compared with the initial solid solution) is 15%. The method of more or less complete prechromatographic separation of fullerenes can be based on the different contents of fullerenes in the initial mixture and solution.

The highest temperature at which the saturation of solution by light fullerenes was performed was 70°C for C_{60} and fullerene solid solution (60 wt % C_{60}, 39 wt % C_{70}, and 1 wt % $C_{76–90}$) and 80°C for C_{70}. At higher temperatures, the spontaneous temperature-initiated noncatalytic (co)polymerization of styrene and fullerenes occurred, which, in particular, caused the destruction of the electronic spectra of fullerenes.

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